B12

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
29 March 2001 (29.03.2001)

PCT

(10) International Publication Number
WO 01/22049 A2

(51) International Patent Classification[7]: G01N

(21) International Application Number: PCT/US00/26138

(22) International Filing Date:
22 September 2000 (22.09.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/155,860 24 September 1999 (24.09.1999) US

(71) Applicants and
(72) Inventors: HALEY, Lawrence, V. [US/CA]; 1 Manju Street, Ottawa, Ontario K1G 4T7 (CA). THEKKADATH, Govindanunny [CA/CA]; 51 E. Bayshore Drive, Nepean, Ontario K2B 6M7 (CA).

(74) Agents: DIGIGLIO, Frank, S. et al.; Scully, Scott, Murphy & Presser, 400 Garden City Plaza, Garden City, NY 11530 (US).

(81) Designated States *(national)*: CA, JP.

(84) Designated States *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:
— *Without international search report and to be republished upon receipt of that report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/22049 A2

(54) Title: A NOVEL ION-MOBILITY BASED DEVICE USING AN OSCILLATORY HIGH-FIELD ION SEPARATOR WITH A MULTI-CHANNEL ARRAY CHARGE COLLECTOR

(57) Abstract: The present invention relates generally to ion mobility spectrometer devices, and particularly, a novel type of ion separator based on the principle of ion mobility separation of molecules in the vapor phase. The proposed device utilizes several interesting characteristics of the behavior of molecular ion motion in a neutral buffer gas under the influence of electric fields. The result is a miniature high-resolution ion generator, separator, and detector that is capable of real-time detection of a range of molecular species in concentrations of parts per billion or less.

BEST AVAILABLE COPY

A NOVEL ION-MOBILITY BASED DEVICE USING AN OSCILLATORY HIGH-FIELD ION SEPARATOR WITH A MULTI-CHANNEL ARRAY CHARGE COLLECTOR

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates generally to ion mobility spectrometer devices, and particularly, a novel type of ion separator based on the principle of ion mobility separation of molecules in the vapor phase. The proposed device utilizes several interesting characteristics of the behavior of molecular ion motion in a neutral buffer gas under the influence of electric fields. The result is a miniature high-resolution ion generator, separator, and detector that is capable of real-time detection of a range of molecular species in concentrations of parts per billion or less.

Description of the Prior Art

Ion Mobility Spectrometry

One of the most practical and successful techniques of ion separation and detection available at present is the mobility separation of charged species produced by ionizing the compounds of interest, separating them in an electric field, and detecting the separated ions using charge collectors and amplifiers. Devices based on Ion Mobility Spectrometers are routinely used in the detection of traces of explosives and drugs by security personnel at airports and other places. The practical realization of this technique of ion separation takes on many forms, but in general they all depend on injecting spatially discrete packets of ions into a buffer gas in which an electric field is present. As the charge packet of ions enter the electric field, their collision limited velocities due to the interaction of the field with the charge gets determined as:

$$v = K E \quad \text{---------- (1)}$$

where v is the velocity of the ion in the electric field E and K is its mobility. The mobility of an ion depends in a complex way on its mass, size, shape, and its interaction with the electric field. An ion of a certain compound is characterized by its mobility, and therefore, when the ions travel towards the detector, they get separated into packets whose arrival times at the detector are characteristic of the corresponding compounds. This gives rise to the ion mobility spectrum and such devices using the mobility separation technique are called ion mobility spectrometers (IMS).

The Classical IMS

As shown in Figure 1, the classical IMS sensor is constructed of a series of stacked rings separated by insulator elements, a gate, a decoupling screen, an electrometer, and an ion source.

The rings are connected electronically by resistors to form an ion accelerator, and any ions formed within the accelerator are focused into a tight beam and accelerated along a voltage gradient from one end to the other. The rings range in size from a cm diameter to up to 10 cm with a thickness of a mm or more. A voltage of 2000 to 4000 volts DC (positive or negative) is applied along the length of accelerator to establish a driving voltage of about 200 volts per cm. This voltage gradient provides the electric drift field for the ions.

The accelerator (sensor) is divided into a reaction and a drift region by a gate. The gate is constructed of two parallel screens (Tyndall gate) or a series of parallel wires of opposite polarity (Nielson-Bradbury). The reaction region ranges in length

from 1 to 5 cm. It houses an ion source (radioisotope, UV, Corona) and any ions formed are prevented from entering the drift region by the gate. Temporarily opening the gate sends a pulse of ions into the drift region for analysis.

A modification of this design has been used by present assignee, IDS Intelligent Detection Systems, Inc., where an ion gun is incorporated in the reaction region that periodically pulses out the ions from the reaction region into the drift region. This avoids the use of a mechanically complicated shutter of the Neilson-Bradbury type and increases the efficiency of utilization of the accumulated ions in the reaction region.

Attached to the reaction region between the gate and the ion source, is a sample injector. The sample is carried, usually by means of an ultrapure gas stream, through the injector, then through the ion source. Product ions are formed which are characteristic of the material injected. The sample injector may employ a membrane to prevent the ambient air from entering the sensor. Continuous sampling is possible with a membrane, which reduces moisture and ammonia interference. The injector may be heated to 300 C, to prevent sample adsorption on the injector wall, to facilitate throughput of poorly volatile materials, to increase analysis speed, to reduce background buildup, and to reduce clustering effects due to high moisture levels and impurities.

The sample is ionized by the reactant ions from the source. A variety of molecular and ion fragments result, governed by the ion chemistry and reaction time (the nature of the ion source, the sample components, the time spent in the reaction region etc.). The ions are pulsed into the drift region by opening the gate for about 0.2 ms. The drift region is normally from 2-10 cm

long and is defined as the region between the gate and the aperture grid. The electrometer detector is located adjacent to the aperture grid. Ion-molecule reactions effectively cease in the drift region and the ionic species more or less maintain their identity during transit. Ions move at a speed (mobility) governed by a mass and the applied voltage gradient. The spectrum (ionogram) observed is roughly characteristic of the substance being analyzed and is used for identification purposes. Various signal processing methods have been employed to analyze overlapping peaks, subtract background, compare to fragmentation patterns to a lookup library for species identification, and to automatically correct for temperature and pressure effects by comparison against a reference.

The drift region is continuously purged with ultrapure nitrogen or air that enters the sensor at the electrometer plate and exits at the high voltage end of the accelerator. The ultrapure gas prevents the sample from entering the drift region (stops any reactions in progress) and purges it from the reactant region. It removes adsorbed impurities (background) and keeps the sensor clean. Ultrapure gas is often employed to carry the sample through the injector into the sensor.

The sensor is hermetically sealed to prevent entry of ambient air. The enclosure is wrapped with a heater and insulation if operation at elevated temperatures is required. Surrounding the sensor are various electronic modules for generating high voltage, gate control, temperature sensing and control, signal amplification and signal processing. Signal processing and intelligence may be onboard or in an external PC.

To summarize operation, ions are generated by the source. These ions react with the sample molecules to form product ions

(molecular ions or fragments). The product ions are moved by the voltage gradient to the control grid where they are neutralized. Every 20 to 30 ms the control grid opens for about 0.2 ms to allow a pulse of ions to enter the drift region. In the drift region the ions are again moved by the voltage gradient towards the aperture grid and the electrometer detector. During transit, the product ions travel at speeds, roughly proportional to their mass and arrive at the electrometer plate at different times (5 to 30 ms). The pattern of transit times (mobility) of all the ions produced from a specific sample molecule is a useful tool for identifying the molecule.

Advantages and Disadvantages of the Classical IMS

Ion mobility spectrometers have become very attractive as simple, compact, and highly sensitive detectors of a large range of compounds that give rise to either positive or negative ionic species. Their advantage over mass spectrometers lies in the fact that no vacuum is necessary for the separation of the charged species, so they avoid the use of complex vacuum pump systems. They are also ideal as detectors for gas chromatographic (GC) columns because the separated output from the columns can be coupled without any losses to the input of the IMS and each eluted portion further analyzed in real time using the relatively fast scanning times (milliseconds) of the IMS compared to the elution times (seconds) of the GC column. However, the one big disadvantage of the IMS with respect to the mass spectrometer is its low resolution. A typical IMS has a resolution of about 15 to 30 compared to resolutions of hundreds for a typical time-of-flight (TOF) mass spectrometer. The resolution of the IMS can only be improved by increasing the drift length of the ions, and this in turn makes the IMS apparatus bulky. Increasing the resolution of the IMS has

several advantages including the obvious increased selectivity, increased sensitivity due to better signal to noise ratios, and better identification of the ion species due to the higher resolution spectrogram. It is highly desirable therefore to explore ways of increasing the resolution of the ion mobility separation technique without increasing the size of the IMS device. Two ways of tackling this problem are by using an oscillatory electric field to increase the apparent drift length of the IMS and by exploiting the change in the mobility of the gaseous ions when the electric fields used for ion drift are increased much beyond the magnitudes used in a classical IMS.

Field Ion Spectrometry or Field Asymmetric Ion Spectrometry (FIS or FAIMS)

The IMS devices that are currently used in practice have electric fields E in the range of 200 to 300 V/cm. The mobility K in these devices can be considered to be independent of the electric field as given by equation (1). However, when the electric fields are substantially higher, equation (1) becomes more complex and the mobility K becomes a function of the electric field. The dependence of mobility on electric field has been previously recognized and exploited in a transverse field IMS by Groshkov in 1988 (Russian Inventor's Certificate No. 966583) and in an ion separation device called the Field Ion Spectrometer (FIS) by Carnahan and Tarassov in 1994 (U.S. Patent No. 5420424). In these cases an oscillatory transverse electric field with asymmetric amplitude impressed across two electrodes was used to vary the mobility of the ions and thus separate them while the ions traveled in a gas flow between the electrodes in a direction perpendicular to the field. Detection of different ions with different masses was accomplished by biasing one electrode with

respect to the other and then varying either the frequency of the scanning field or the bias potential or both.

Description of an FIS

A prior art device know as the FIS sensor is presented in Figure 2 which is shown as comprising two concentric tubes, the inner and the outer electrode, separated by a few millimeters. The overall length is approximately 12 cm, and the diameter is approximately 4 cm at the largest part. The inlet is stainless steel and Teflon. It houses a nickel-63 radioisotope source at one end and the Teflon injector is located at the outer end of the inlet. The insulator electrically isolates the stainless steel portion of the injector that carries an electrical charge of approximately 250 volts. The insulator also facilitates sample injection.

The inlet is equipped with a heater and a temperature sensor to raise the operating temperature to approximately 150_ C. The higher temperatures facilitate the injection of poorly volatile samples and assist with sample cleanout.

The ionizer electrode is charged electrically (<350 V) and deflects any ions in the vicinity of the region around the radioisotope source and may be sample ions of reactant ions resulting from ionization of the air present.

Once inside the ion filter, the ions are moved towards the electrometer by means of a 1.5 liter per minute airflow from the clean air supply. The clean air supply is recirculated air from the sensor exhaust, which is passed through filters by means of an air pump. Part of the clean air passes through the ion filter and part, 2.0 liters per minute, passes through the inner

electrode past the ionizer electrode. This part of the clean air supply purges the sensor of any sample present and prevents the sample or impurities present from entering the ion filter where they may interfere with performance and contaminate the area.

The sample out airflow and the carrier air out flows are adjusted to provide a small suction at the sample inlet to draw any sample present to the ionization region.

The outer electrode is grounded and a high frequency *asymmetric* RF voltage is applied to the inner electrode. The RF voltage is adjustable from 1500 to about 4000 volts and can be negative or positive in polarity. An offset compensation voltage of 0 to 50 volts positive or negative is also applied to the inner electrode to off set the applied RF voltage. If positive ions are being investigated, the RF voltage is normally positive and the compensation voltage negative, while the ionizer voltage is positive. The opposite is true for negative ions (explosives).

To summarize operation, the sample is injected and moves to the radioisotope source where it is ionized, then deflected into the ion filter. In the ion filter it is carried to the electrometer by the low velocity airflow. While in the ion filter, the RF voltage drives the ions towards the inner or the outer electrode where it may be collected and discharged. To prevent this, a compensation voltage is required for each ion and a scan of compensation voltages will generate a spectrum of ions or an ionagram. The compensation voltage for each ion peak is noted and a pattern of peaks characteristic of the particular ion is established. Varying the dispersion voltage and the resolution voltage changes the pattern, providing more information about the ions present, or separating overlapping peaks. A wide range of

operating conditions is possible to increase the selectivity of FIS over IMS.

Disadvantages of the FIS Detector

There are two main disadvantages to the FIS detector that overweigh its high sensitivity in the mass filter detection mode. In the first instance, even though the FIS sensor has apparently a high sensitivity, it is achieved at the expense of scanning time. The IDS IMS (manufactured by Intelligent Detection Systems, Inc., Nepean, Canada) for example scans for all explosive compounds in less than two milliseconds. This is about ten thousand times faster than a typical FIS scan of 20 seconds for several compounds. Thus the FIS sensor is a poor companion to a fast GC when compared to the IDS IMS. Despite the mass filtering mode of operation of the FIS, the ultimate sensitivity of all the ion detection devices that operate in the chemical ionization mode is limited by the rate of reactions producing the final detectable species, and these reactions are comparatively slow for explosive molecules like RDX and PETN.

The second disadvantage of the FIS sensor is the way ions are transported down the drift tube on their way to the charge detector plates. This transport relies solely on the mass flow of the carrier gas down the tube and thus becomes sensitive to any variations in the flow rate, turbulence, and other mass flow characteristics. A true ion transport drift field which increases the drift velocity to a high enough value that mass flow velocities become independent is necessary in order to avoid the flow dependency of the ions for transport. This is however, not possible in the FIS due to the nature of its design.

Summary of the Invention

The Improved Ion Separator and Detector

The present invention relates to a new type of ion separator and detector which separates the ions based on the variation of their mobilities in high electric fields and which greatly improves on the FIS sensor by overcoming the disadvantages as mentioned above.

Brief Description of the Drawings

Preferred embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a schematic diagram depicting a conventional IMS device.

Figure 2 is a schematic diagram depicting the prior art FIS device.

Figure 3 is a schematic diagram depicting the novel ion separator and multi-channel detector of the invention.

Detailed Description of the Preferred Embodiment

Figure 3 is a schematic diagram depicting the novel Ion Separator and Detector of the invention. Particularly, the novel Ion Separator and Detector is a oscillatory, high field separator device implementing a combination of transverse and longitudinal electric fields. As shown in Figure 3, the electrodes 1 and 2 create these two fields. These electrodes are two metallic

plates that are *at an angle to each other* rather than parallel to each other as in the FIS design. They are also curved inward with the concave surfaces encompassing the drift region. The curvature assists in focusing the ion beam towards the middle of the drift region. There are two voltages impressed on these plates; plate 1 has a DC voltage applied to it (typically 1 to 100 volts) which is fixed when a scan takes place but which can be changed to another voltage to vary the scale of the scan. Electrode 2 has a *symmetric* time varying periodic potential applied to it which can be a sine wave, a square wave, a triangular wave, or any such of the general form

$V2(t) = A\,f(t)$ for $t = nT$ to $t = nT + T/2$
and $V2(t) = -A\,f(t)$ for $t = nT+T/2$ to $t = (n+1)T$
where $n = 0, 1, 2, \ldots$.

Note that the waveform is symmetric, and not asymmetric as in the FIS. This greatly simplifies the construction of the electronics necessary to generate the waveform.

At the narrow end at left there is a means for introducing an ionized stream of sample and injecting them into the region between the two plates. This injection is normally done by using an electric field between two electrodes by biasing them appropriately with positive or negative voltages. The creation of the ion stream or ion packet can be done by any appropriate means, for example, using a radioactive nickel source as in an IMS, a photoionization source, a laser ionization source, a corona or spark gap ionization source, a field ionization source, etc. At the wide end of the plates is an array of collectors numbering typically a few tens to a few hundreds depending on the needed resolution and overall size of the device. This array consists of a series of pin electrodes, typically square in cross

section, spaced close to each other in a straight line and having a common high shield electrode 3 surrounding the pins. The shield electrode can be biased at a higher voltage than the pins to isolate them from the induced current effects of the approaching ion stream. The geometrical construction of the electrode array is important in determining the resolution and sensitivity of the instrument but here we describe an illustrative case only.

A means for introducing a neutral buffer gas is provided preferably at the detector array end of the device with a corresponding gas exit at the ion source end. This arrangement keeps the drift region clean of un-ionized sample and other impurities that could react with the drifting sample ions. This aspect of the detector is also different from the FIS detector because we do not depend on mass transport of the sample ions towards the collector but rather on the drift under the influence of the transverse electric field as explained in the next paragraph. The electrodes and the gas inlets and outlets are enclosed in a sealed metallic outer container (which is not shown in the figure) to prevent electromagnetic radiation from escaping the device and causing interference. The necessary signals and electric power are routed using shielded cables into and out of the container.

Because of this inclination of one plate to the other, the electric field between the two plates will have two components as shown in the figure; one component (E2(t)) in the vertical direction and one (E3(t)) in the horizontal direction towards the array charge collector assembly at right. The horizontal component of the electric field does the work of the drift field in a conventional IMS for transporting the ions towards the detector. This component will oscillate between a maximum value

of E3cos(theta) and 0, where theta is the half angle between the two plates and is typically 1 to 10 degrees. The direction of the electric field is always towards the charge collector array. However, as the ion packets travel down the drift region, it meets the oscillatory transverse electric field as in the FIS. This field in effect increases the path length of the ions in the drift region with a net result of increasing the resolution of the device without increasing its actual physical length. In addition, the use of a high electric field would bring into play the non-linear characteristics of the mobility of different ion types for help in their separation. Thus this design utilizes the advantages of the separation afforded by the non-linear effects of electric field on mobility with the added advantage of transporting the ions using a true drift field rather that flow transport as in the FIS.

The problem of long detection times in the FIS due to the sweeping of the transverse electric field will be addressed in the new proposed device by using multiple detectors. Thus the proposed device will act as several FIS-like sensors in parallel. As the ions oscillate when they travel down the drift region, they are separated as a complex function of their dependence on mass, shape, and the electric field to which they are subjected. Because of the presence of the additional field created by the non-oscillating electrode, the ions will be transversely separated and will arrive at the farther end at different heights from the lower electrode with the oscillating voltage. This separation is exploited to position a row of Faraday-cup-style shielded detector pins at the detection end of the system to collect the ions and measure their currents. Thus we have in effect a multi-channel detector array for the simultaneous detection of the ions that eliminates the need for a sweep voltage to serialize the detection of ions as is done in the FIS.

Thus, as described herein, the new ion separator and detector device is an improved, higher resolution ion mobility based sensor having superior characteristics to the existing devices using the dependence of ion mobility on electric field. The improvements are possible by a novel design of the drift field and ion collector parts of the device. The new design makes it possible to use a true drift field to transport the ions and an array of detectors to collect and measure the ion current of the ions separated by an oscillating transverse field. This makes the device able to simultaneously measure the currents due to different species without having to resort to a sweep voltage to measure each species one after the other as done in the FAIMS. The resolution is improved because of the increased drift length due to the oscillatory nature of the electric field and because of the non-linear field dependence of mobility of the sample ions on the electric field.

While the invention has been particularly shown and described with respect to a preferred embodiment thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit and scope of the invention.

We Claim:

1. An ion mobility separator device comprising:

a housing;

first and second electrodes positioned within said housing and disposed at an angle with respect to each other and defining a narrow end, a wide end, and a drift region therebetween;

means located at said narrow end for ionizing a sample to be detected and introducing an ionized packet stream into said drift region;

detector array means disposed at said wide end for receiving ion packets of said ionized packet stream;

means for impressing a constant voltage to one of said first and second electrodes for creating an electric field between said first and second electrodes, said electric field having a vertical component for transversely separating ions in said ionized sample stream;

means for impressing a periodic voltage to another of said first and second electrodes for generating an oscillatory transverse electric field, said oscillatory transverse electric field effectively increases a path length of ions in said drift region, thereby increasing resolution of said device.

2. The ion mobility device as claimed in Claim 1, wherein said periodic voltage is a symmetric voltage waveform.

3. The ion mobility device as claimed in Claim 1, wherein a half-angle between said first and second electrodes ranges anywhere between 1° degrees - 10° degrees.

4. The ion mobility device as claimed in Claim 1, wherein said electric field further includes a horizontal component directed toward said detector array means

5. The ion mobility device as claimed in Claim 1, further including means for introducing a buffer gas in said drift region, said means including a gas inlet and gas outlet means.

6. The ion mobility device as claimed in Claim 1, wherein said means for ionizing a sample to be detected includes one selected from a group comprising: a radioactive nickel source, a photoionization source, a laser ionization source, a spark gap ionization source, and, a field ionization source.

7. The ion mobility device as claimed in Claim 1, wherein each said first and second electrodes are curved having concave surfaces encompassing said drift region.

8. The ion mobility device as claimed in Claim 1, wherein said detector array means includes detector pins, said device further including electrode means surrounding said pins.

9. The ion mobility device as claimed in Claim 8, wherein said detector pins are square shaped.

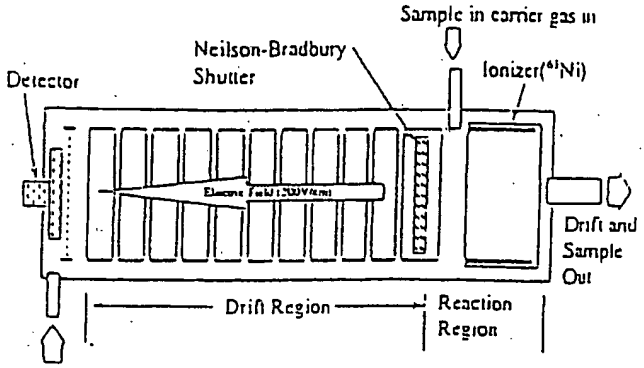

Figure 1 Schematic diagram of a segmented ring IMS

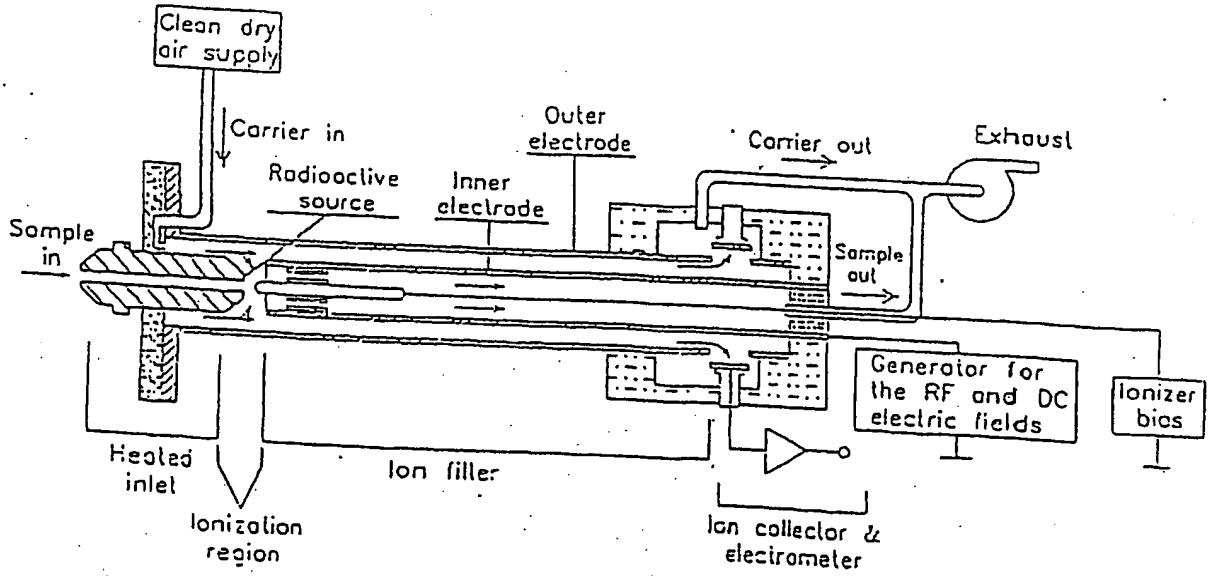

Figure 2 Schematic diagram of an FIS sensor

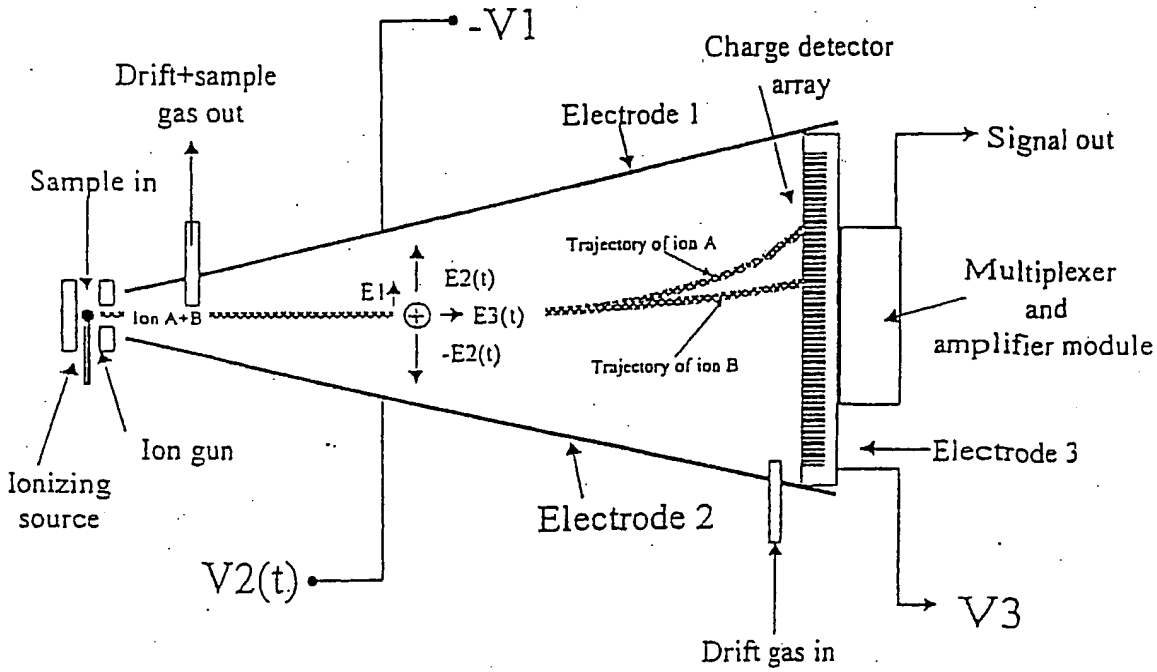

Figure 3 Schematic diagram of the new ion separator and multi-channel detector

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

CORRECTED VERSION

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
29 March 2001 (29.03.2001)

PCT

(10) International Publication Number
WO 01/022049 A2

(51) International Patent Classification[7]: G01N

(21) International Application Number: PCT/US00/26138

(22) International Filing Date:
22 September 2000 (22.09.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/155,860 24 September 1999 (24.09.1999) US

(71) Applicants and
(72) Inventors: **HALEY, Lawrence, V.** [US/CA]; 1 Manju Street, Ottawa, Ontario K1G 4T7 (CA). **THEKKADATH, Govindanunny** [CA/CA]; 51 E. Bayshore Drive, Nepean, Ontario K2B 6M7 (CA).

(74) Agents: **DIGIGLIO, Frank, S.** et al.; Scully, Scott, Murphy & Presser, 400 Garden City Plaza, Garden City, NY 11530 (US).

(81) Designated States *(national)*: CA, JP.

(84) Designated States *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:
— *without international search report and to be republished upon receipt of that report*

(48) Date of publication of this corrected version:
3 October 2002

(15) Information about Correction:
see PCT Gazette No. 40/2002 of 3 October 2002, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/022049 A2

(54) Title: A NOVEL ION-MOBILITY BASED DEVICE USING AN OSCILLATORY HIGH-FIELD ION SEPARATOR WITH A MULTI-CHANNEL ARRAY CHARGE COLLECTOR

(57) Abstract: The present invention relates generally to ion mobility spectrometer devices, and particularly, a novel type of ion separator based on the principle of ion mobility separation of molecules in the vapor phase. The proposed device utilizes several interesting characteristics of the behavior of molecular ion motion in a neutral buffer gas under the influence of electric fields. The result is a miniature high-resolution ion generator, separator, and detector that is capable of real-time detection of a range of molecular species in concentrations of parts per billion or less.

A NOVEL ION-MOBILITY BASED DEVICE USING AN OSCILLATORY HIGH-FIELD ION SEPARATOR WITH A MULTI-CHANNEL ARRAY CHARGE COLLECTOR

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates generally to ion mobility spectrometer devices, and particularly, a novel type of ion separator based on the principle of ion mobility separation of molecules in the vapor phase. The proposed device utilizes several interesting characteristics of the behavior of molecular ion motion in a neutral buffer gas under the influence of electric fields. The result is a miniature high-resolution ion generator, separator, and detector that is capable of real-time detection of a range of molecular species in concentrations of parts per billion or less.

Description of the Prior Art

Ion Mobility Spectrometry

One of the most practical and successful techniques of ion separation and detection available at present is the mobility separation of charged species produced by ionizing the compounds of interest, separating them in an electric field, and detecting the separated ions using charge collectors and amplifiers. Devices based on Ion Mobility Spectrometers are routinely used in the detection of traces of explosives and drugs by security personnel at airports and other places. The practical realization of this technique of ion separation takes on many forms, but in general they all depend on injecting spatially discrete packets of ions into a buffer gas in which an electric field is present. As the charge packet of ions enter the electric field, their collision limited velocities due to the interaction of the field with the charge gets determined as:

$$v = K E \quad \text{----------} \quad (1)$$

where v is the velocity of the ion in the electric field E and K is its mobility. The mobility of an ion depends in a complex way on its mass, size, shape, and its interaction with the electric field. An ion of a certain compound is characterized by its mobility, and therefore, when the ions travel towards the detector, they get separated into packets whose arrival times at the detector are characteristic of the corresponding compounds. This gives rise to the ion mobility spectrum and such devices using the mobility separation technique are called ion mobility spectrometers (IMS).

The Classical IMS .

As shown in Figure 1, the classical IMS sensor is constructed of a series of stacked rings separated by insulator elements, a gate, a decoupling screen, an electrometer, and an ion source.

The rings are connected electronically by resistors to form an ion accelerator, and any ions formed within the accelerator are focused into a tight beam and accelerated along a voltage gradient from one end to the other. The rings range in size from a cm diameter to up to 10 cm with a thickness of a mm or more. A voltage of 2000 to 4000 volts DC (positive or negative) is applied along the length of accelerator to establish a driving voltage of about 200 volts per cm. This voltage gradient provides the electric drift field for the ions.

The accelerator (sensor) is divided into a reaction and a drift region by a gate. The gate is constructed of two parallel screens (Tyndall gate) or a series of parallel wires of opposite polarity (Nielson-Bradbury). The reaction region ranges in length

from 1 to 5 cm. It houses an ion source (radioisotope, UV, Corona) and any ions formed are prevented from entering the drift region by the gate. Temporarily opening the gate sends a pulse of ions into the drift region for analysis.

A modification of this design has been used by present assignee, IDS Intelligent Detection Systems, Inc., where an ion gun is incorporated in the reaction region that periodically pulses out the ions from the reaction region into the drift region. This avoids the use of a mechanically complicated shutter of the Neilson-Bradbury type and increases the efficiency of utilization of the accumulated ions in the reaction region.

Attached to the reaction region between the gate and the ion source, is a sample injector. The sample is carried, usually by means of an ultrapure gas stream, through the injector, then through the ion source. Product ions are formed which are characteristic of the material injected. The sample injector may employ a membrane to prevent the ambient air from entering the sensor. Continuous sampling is possible with a membrane, which reduces moisture and ammonia interference. The injector may be heated to 300 C, to prevent sample adsorption on the injector wall, to facilitate throughput of poorly volatile materials, to increase analysis speed, to reduce background buildup, and to reduce clustering effects due to high moisture levels and impurities.

The sample is ionized by the reactant ions from the source. A variety of molecular and ion fragments result, governed by the ion chemistry and reaction time (the nature of the ion source, the sample components, the time spent in the reaction region etc.). The ions are pulsed into the drift region by opening the gate for about 0.2 ms. The drift region is normally from 2-10 cm

long and is defined as the region between the gate and the aperture grid. The electrometer detector is located adjacent to the aperture grid. Ion-molecule reactions effectively cease in the drift region and the ionic species more or less maintain their identity during transit. Ions move at a speed (mobility) governed by a mass and the applied voltage gradient. The spectrum (ionogram) observed is roughly characteristic of the substance being analyzed and is used for identification purposes. Various signal processing methods have been employed to analyze overlapping peaks, subtract background, compare to fragmentation patterns to a lookup library for species identification, and to automatically correct for temperature and pressure effects by comparison against a reference.

The drift region is continuously purged with ultrapure nitrogen or air that enters the sensor at the electrometer plate and exits at the high voltage end of the accelerator. The ultrapure gas prevents the sample from entering the drift region (stops any reactions in progress) and purges it from the reactant region. It removes adsorbed impurities (background) and keeps the sensor clean. Ultrapure gas is often employed to carry the sample through the injector into the sensor.

The sensor is hermetically sealed to prevent entry of ambient air. The enclosure is wrapped with a heater and insulation if operation at elevated temperatures is required. Surrounding the sensor are various electronic modules for generating high voltage, gate control, temperature sensing and control, signal amplification and signal processing. Signal processing and intelligence may be onboard or in an external PC.

To summarize operation, ions are generated by the source. These ions react with the sample molecules to form product ions

(molecular ions or fragments). The product ions are moved by the voltage gradient to the control grid where they are neutralized. Every 20 to 30 ms the control grid opens for about 0.2 ms to allow a pulse of ions to enter the drift region. In the drift region the ions are again moved by the voltage gradient towards the aperture grid and the electrometer detector. During transit, the product ions travel at speeds, roughly proportional to their mass and arrive at the electrometer plate at different times (5 to 30 ms). The pattern of transit times (mobility) of all the ions produced from a specific sample molecule is a useful tool for identifying the molecule.

Advantages and Disadvantages of the Classical IMS

Ion mobility spectrometers have become very attractive as simple, compact, and highly sensitive detectors of a large range of compounds that give rise to either positive or negative ionic species. Their advantage over mass spectrometers lies in the fact that no vacuum is necessary for the separation of the charged species, so they avoid the use of complex vacuum pump systems. They are also ideal as detectors for gas chromatographic (GC) columns because the separated output from the columns can be coupled without any losses to the input of the IMS and each eluted portion further analyzed in real time using the relatively fast scanning times (milliseconds) of the IMS compared to the elution times (seconds) of the GC column. However, the one big disadvantage of the IMS with respect to the mass spectrometer is its low resolution. A typical IMS has a resolution of about 15 to 30 compared to resolutions of hundreds for a typical time-of-flight (TOF) mass spectrometer. The resolution of the IMS can only be improved by increasing the drift length of the ions, and this in turn makes the IMS apparatus bulky. Increasing the resolution of the IMS has

several advantages including the obvious increased selectivity, increased sensitivity due to better signal to noise ratios, and better identification of the ion species due to the higher resolution spectrogram. It is highly desirable therefore to explore ways of increasing the resolution of the ion mobility separation technique without increasing the size of the IMS device. Two ways of tackling this problem are by using an oscillatory electric field to increase the apparent drift length of the IMS and by exploiting the change in the mobility of the gaseous ions when the electric fields used for ion drift are increased much beyond the magnitudes used in a classical IMS.

Field Ion Spectrometry or Field Asymmetric Ion Spectrometry (FIS or FAIMS)

The IMS devices that are currently used in practice have electric fields E in the range of 200 to 300 V/cm. The mobility K in these devices can be considered to be independent of the electric field as given by equation (1). However, when the electric fields are substantially higher, equation (1) becomes more complex and the mobility K becomes a function of the electric field. The dependence of mobility on electric field has been previously recognized and exploited in a transverse field IMS by Groshkov in 1988 (Russian Inventor's Certificate No. 966583) and in an ion separation device called the Field Ion Spectrometer (FIS) by Carnahan and Tarassov in 1994 (U.S. Patent No. 5420424). In these cases an oscillatory transverse electric field with asymmetric amplitude impressed across two electrodes was used to vary the mobility of the ions and thus separate them while the ions traveled in a gas flow between the electrodes in a direction perpendicular to the field. Detection of different ions with different masses was accomplished by biasing one electrode with

respect to the other and then varying either the frequency of the scanning field or the bias potential or both.

Description of an FIS

A prior art device know as the FIS sensor is presented in Figure 2 which is shown as comprising two concentric tubes, the inner and the outer electrode, separated by a few millimeters. The overall length is approximately 12 cm, and the diameter is approximately 4 cm at the largest part. The inlet is stainless steel and Teflon. It houses a nickel-63 radioisotope source at one end and the Teflon injector is located at the outer end of the inlet. The insulator electrically isolates the stainless steel portion of the injector that carries an electrical charge of approximately 250 volts. The insulator also facilitates sample injection.

The inlet is equipped with a heater and a temperature sensor to raise the operating temperature to approximately 150_ C. The higher temperatures facilitate the injection of poorly volatile samples and assist with sample cleanout.

The ionizer electrode is charged electrically (<350 V) and deflects any ions in the vicinity of the region around the radioisotope source and may be sample ions of reactant ions resulting from ionization of the air present.

Once inside the ion filter, the ions are moved towards the electrometer by means of a 1.5 liter per minute airflow from the clean air supply. The clean air supply is recirculated air from the sensor exhaust, which is passed through filters by means of an air pump. Part of the clean air passes through the ion filter and part, 2.0 liters per minute, passes through the inner

electrode past the ionizer electrode. This part of the clean air supply purges the sensor of any sample present and prevents the sample or impurities present from entering the ion filter where they may interfere with performance and contaminate the area.

The sample out airflow and the carrier air out flows are adjusted to provide a small suction at the sample inlet to draw any sample present to the ionization region.

The outer electrode is grounded and a high frequency *asymmetric* RF voltage is applied to the inner electrode. The RF voltage is adjustable from 1500 to about 4000 volts and can be negative or positive in polarity. An offset compensation voltage of 0 to 50 volts positive or negative is also applied to the inner electrode to off set the applied RF voltage. If positive ions are being investigated, the RF voltage is normally positive and the compensation voltage negative, while the ionizer voltage is positive. The opposite is true for negative ions (explosives).

To summarize operation, the sample is injected and moves to the radioisotope source where it is ionized, then deflected into the ion filter. In the ion filter it is carried to the electrometer by the low velocity airflow. While in the ion filter, the RF voltage drives the ions towards the inner or the outer electrode where it may be collected and discharged. To prevent this, a compensation voltage is required for each ion and a scan of compensation voltages will generate a spectrum of ions or an ionagram. The compensation voltage for each ion peak is noted and a pattern of peaks characteristic of the particular ion is established. Varying the dispersion voltage and the resolution voltage changes the pattern, providing more information about the ions present, or separating overlapping peaks. A wide range of

operating conditions is possible to increase the selectivity of FIS over IMS.

Disadvantages of the FIS Detector

There are two main disadvantages to the FIS detector that overweigh its high sensitivity in the mass filter detection mode. In the first instance, even though the FIS sensor has apparently a high sensitivity, it is achieved at the expense of scanning time. The IDS IMS (manufactured by Intelligent Detection Systems, Inc., Nepean, Canada) for example scans for all explosive compounds in less than two milliseconds. This is about ten thousand times faster than a typical FIS scan of 20 seconds for several compounds. Thus the FIS sensor is a poor companion to a fast GC when compared to the IDS IMS. Despite the mass filtering mode of operation of the FIS, the ultimate sensitivity of all the ion detection devices that operate in the chemical ionization mode is limited by the rate of reactions producing the final detectable species, and these reactions are comparatively slow for explosive molecules like RDX and PETN.

The second disadvantage of the FIS sensor is the way ions are transported down the drift tube on their way to the charge detector plates. This transport relies solely on the mass flow of the carrier gas down the tube and thus becomes sensitive to any variations in the flow rate, turbulence, and other mass flow characteristics. A true ion transport drift field which increases the drift velocity to a high enough value that mass flow velocities become independent is necessary in order to avoid the flow dependency of the ions for transport. This is however, not possible in the FIS due to the nature of its design.

Summary of the Invention

The Improved Ion Separator and Detector

The present invention relates to a new type of ion separator and detector which separates the ions based on the variation of their mobilities in high electric fields and which greatly improves on the FIS sensor by overcoming the disadvantages as mentioned above.

Brief Description of the Drawings

Preferred embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a schematic diagram depicting a conventional IMS device.

Figure 2 is a schematic diagram depicting the prior art FIS device.

Figure 3 is a schematic diagram depicting the novel ion separator and multi-channel detector of the invention.

Detailed Description of the Preferred Embodiment

Figure 3 is a schematic diagram depicting the novel Ion Separator and Detector of the invention. Particularly, the novel Ion Separator and Detector is a oscillatory, high field separator device implementing a combination of transverse and longitudinal electric fields. As shown in Figure 3, the electrodes 1 and 2 create these two fields. These electrodes are two metallic

plates that are *at an angle to each other* rather than parallel to each other as in the *FIS* design. They are also curved inward with the concave surfaces encompassing the drift region. The curvature assists in focusing the ion beam towards the middle of the drift region. There are two voltages impressed on these plates; plate 1 has a DC voltage applied to it (typically 1 to 100 volts) which is fixed when a scan takes place but which can be changed to another voltage to vary the scale of the scan. Electrode 2 has a *symmetric* time varying periodic potential applied to it which can be a sine wave, a square wave, a triangular wave, or any such of the general form

$V2(t) = A\,f(t)$ for $t = nT$ to $t = nT + T/2$
and $V2(t) = -A\,f(t)$ for $t = nT+T/2$ to $t = (n+1)T$
where $n = 0, 1, 2, \ldots$.

Note that the waveform is symmetric, and not asymmetric as in the FIS. This greatly simplifies the construction of the electronics necessary to generate the waveform.

At the narrow end at left there is a means for introducing an ionized stream of sample and injecting them into the region between the two plates. This injection is normally done by using an electric field between two electrodes by biasing them appropriately with positive or negative voltages. The creation of the ion stream or ion packet can be done by any appropriate means, for example, using a radioactive nickel source as in an IMS, a photoionization source, a laser ionization source, a corona or spark gap ionization source, a field ionization source, etc. At the wide end of the plates is an array of collectors numbering typically a few tens to a few hundreds depending on the needed resolution and overall size of the device. This array consists of a series of pin electrodes, typically square in cross

section, spaced close to each other in a straight line and having a common high shield electrode 3 surrounding the pins. The shield electrode can be biased at a higher voltage than the pins to isolate them from the induced current effects of the approaching ion stream. The geometrical construction of the electrode array is important in determining the resolution and sensitivity of the instrument but here we describe an illustrative case only.

A means for introducing a neutral buffer gas is provided preferably at the detector array end of the device with a corresponding gas exit at the ion source end. This arrangement keeps the drift region clean of un-ionized sample and other impurities that could react with the drifting sample ions. This aspect of the detector is also different from the FIS detector because we do not depend on mass transport of the sample ions towards the collector but rather on the drift under the influence of the transverse electric field as explained in the next paragraph. The electrodes and the gas inlets and outlets are enclosed in a sealed metallic outer container (which is not shown in the figure) to prevent electromagnetic radiation from escaping the device and causing interference. The necessary signals and electric power are routed using shielded cables into and out of the container.

Because of this inclination of one plate to the other, the electric field between the two plates will have two components as shown in the figure; one component (E2(t)) in the vertical direction and one (E3(t)) in the horizontal direction towards the array charge collector assembly at right. The horizontal component of the electric field does the work of the drift field in a conventional IMS for transporting the ions towards the detector. This component will oscillate between a maximum value

of E3cos(theta) and 0, where theta is the half angle between the two plates and is typically 1 to 10 degrees. The direction of the electric field is always towards the charge collector array. However, as the ion packets travel down the drift region, it meets the oscillatory transverse electric field as in the FIS. This field in effect increases the path length of the ions in the drift region with a net result of increasing the resolution of the device without increasing its actual physical length. In addition, the use of a high electric field would bring into play the non-linear characteristics of the mobility of different ion types for help in their separation. Thus this design utilizes the advantages of the separation afforded by the non-linear effects of electric field on mobility with the added advantage of transporting the ions using a true drift field rather that flow transport as in the FIS.

The problem of long detection times in the FIS due to the sweeping of the transverse electric field will be addressed in the new proposed device by using multiple detectors. Thus the proposed device will act as several FIS-like sensors in parallel. As the ions oscillate when they travel down the drift region, they are separated as a complex function of their dependence on mass, shape, and the electric field to which they are subjected. Because of the presence of the additional field created by the non-oscillating electrode, the ions will be transversely separated and will arrive at the farther end at different heights from the lower electrode with the oscillating voltage. This separation is exploited to position a row of Faraday-cup-style shielded detector pins at the detection end of the system to collect the ions and measure their currents. Thus we have in effect a multi-channel detector array for the simultaneous detection of the ions that eliminates the need for a sweep voltage to serialize the detection of ions as is done in the FIS.

Thus, as described herein, the new ion separator and detector device is an improved, higher resolution ion mobility based sensor having superior characteristics to the existing devices using the dependence of ion mobility on electric field. The improvements are possible by a novel design of the drift field and ion collector parts of the device. The new design makes it possible to use a true drift field to transport the ions and an array of detectors to collect and measure the ion current of the ions separated by an oscillating transverse field. This makes the device able to simultaneously measure the currents due to different species without having to resort to a sweep voltage to measure each species one after the other as done in the FAIMS. The resolution is improved because of the increased drift length due to the oscillatory nature of the electric field and because of the non-linear field dependence of mobility of the sample ions on the electric field.

While the invention has been particularly shown and described with respect to a preferred embodiment thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit and scope of the invention.

We Claim:

1. An ion mobility separator device comprising:

a housing;

first and second electrodes positioned within said housing and disposed at an angle with respect to each other and defining a narrow end, a wide end, and a drift region therebetween;

means located at said narrow end for ionizing a sample to be detected and introducing an ionized packet stream into said drift region;

detector array means disposed at said wide end for receiving ion packets of said ionized packet stream;

means for impressing a constant voltage to one of said first and second electrodes for creating an electric field between said first and second electrodes, said electric field having a vertical component for transversely separating ions in said ionized sample stream;

means for impressing a periodic voltage to another of said first and second electrodes for generating an oscillatory transverse electric field, said oscillatory transverse electric field effectively increases a path length of ions in said drift region, thereby increasing resolution of said device.

2. The ion mobility device as claimed in Claim 1, wherein said periodic voltage is a symmetric voltage waveform.

3. The ion mobility device as claimed in Claim 1, wherein a half-angle between said first and second electrodes ranges anywhere between 1° degrees - 10° degrees.

4. The ion mobility device as claimed in Claim 1, wherein said electric field further includes a horizontal component directed toward said detector array means

5. The ion mobility device as claimed in Claim 1, further including means for introducing a buffer gas in said drift region, said means including a gas inlet and gas outlet means.

6. The ion mobility device as claimed in Claim 1, wherein said means for ionizing a sample to be detected includes one selected from a group comprising: a radioactive nickel source, a photoionization source, a laser ionization source, a spark gap ionization source, and, a field ionization source.

7. The ion mobility device as claimed in Claim 1, wherein each said first and second electrodes are curved having concave surfaces encompassing said drift region.

8. The ion mobility device as claimed in Claim 1, wherein said detector array means includes detector pins, said device further including electrode means surrounding said pins.

9. The ion mobility device as claimed in Claim 8, wherein said detector pins are square shaped.

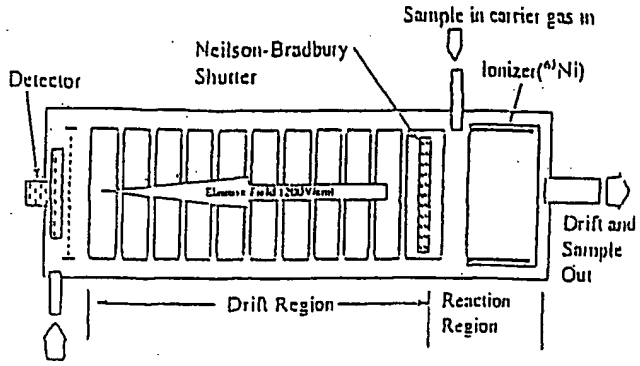

Figure 1 Schematic diagram of a segmented ring IMS

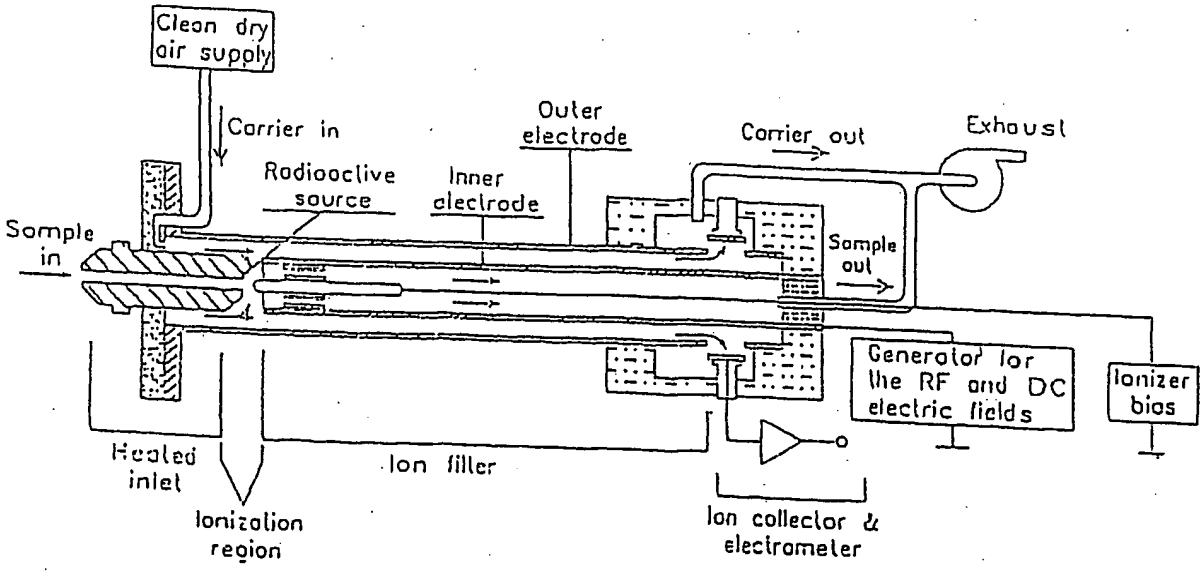

Figure 2 Schematic diagram of an FIS sensor

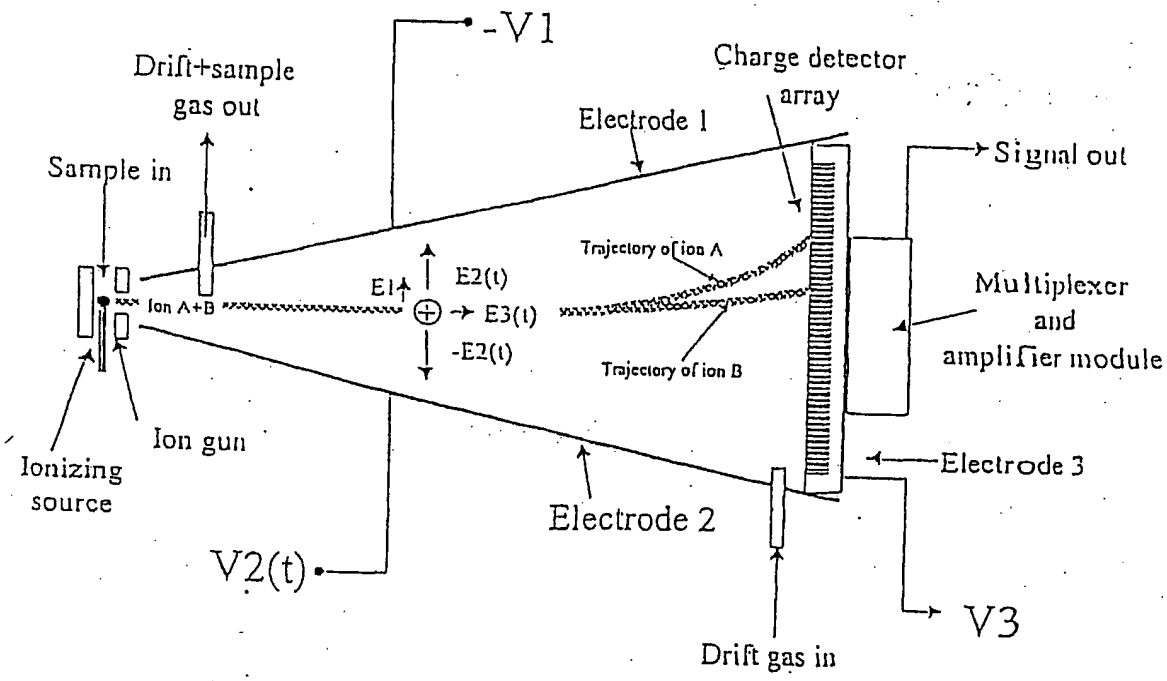

Figure 3 Schematic diagram of the new ion separator and multi-channel detector

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☑ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☑ FADED TEXT OR DRAWING
- ☑ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.
As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.